**Atmospheric
Chemistry
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Discussions**

Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry

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Abstract

Isoprene is an important atmospheric volatile organic compound involved in ozone production and NO_x ($NO+NO_2$) sequestration and transport. Isoprene reaction with OH in the presence of NO can form either isoprene nitrates or convert NO to NO_2 which can photolyze to form ozone. While it has been shown that isoprene nitrate production can represent an important sink for NO_x in forest impacted environments, there is little experimental knowledge of the relative importance of the individual isoprene nitrate isomers, each of which has a different fate and reactivity. In this work, we have identified the 8 individual isomers and determined their total and individual production yields. The overall yield of isoprene nitrates at atmospheric pressure and 295 K was found to be 0.070(+0.025/–0.015). Three isomers, the (4,3)-IN, (1,2)-IN and Z-(4,1)-IN represent 90% of the total IN yield. We also determined the ozone rate constants for three of the isomers, and have calculated their atmospheric lifetimes, which range from ∼1–2 h, making their oxidation products likely more important as atmospheric organic nitrates and sinks for nitrogen.

1 Introduction

Isoprene (2-methyl-1,3-butadiene) is the dominant biogenic volatile organic compound emitted into the atmosphere at 500–750 Tg yr^{-1} (Guenther et al., 2006). Isoprene is emitted by plants and readily reacts with OH radicals, ozone, and NO_3 in the atmosphere (Tuazon and Atkinson, 1990; Chuong and Stevens, 2002; Guenther et al., 2006). Reaction with OH is the dominant pathway for the removal of isoprene during the day ($k=1.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1}) (Atkinson et al., 2006). Reactions (R1–R3) show a simple mechanism for the addition of OH and O_2 to one of the four double-bonded carbons (Reaction R1) to produce either the alkoxy radical and

$$C_5H_8 + OH(+O_2) \rightarrow \cdot O\text{-}O\text{-}C_5H_8\text{-}OH \qquad (R1)$$

$$^{\cdot}O\text{-}O\text{-}C_5H_8\text{-}OH + NO \rightarrow {}^{\cdot}O\text{-}C_5H_8\text{-}OH + NO_2 \tag{R2}$$

$$^{\cdot}O\text{-}O\text{-}C_5H_8\text{-}OH + NO \rightarrow O_2N\text{-}O\text{-}C_5H_8\text{-}OH \tag{R3}$$
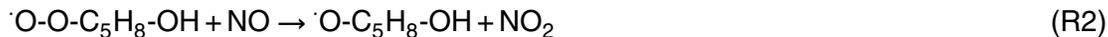
NO_2 (Reaction R2), or a hydroxy nitrate ("isoprene nitrate") (Reaction R3). The NO_2 formed in Reaction (R2) can photolyze to produce ozone (Reactions R4 and R5). Competing with Reactions (R2)

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R4}$$

$$O(^3P) + O_2 \rightarrow O_3 \tag{R5}$$

and 3 is reaction of the hydroxyperoxy radicals with HO_2, to produce organic hydroperoxides, and ultimately, dihydroxyepoxides (Paulot et al., 2009a). However, in the Northern Hemisphere continental environments, the majority of peroxy radicals will react with NO (Barket et al., 2004; Paulot et al., 2009a), and thus the nitrate formation pathways and subsequent chemistry are very important.

Isoprene nitrate (IN) production, according to global modeling studies, has a significant impact on ozone production (Wu et al., 2007). INs act as a sink for NO_x ($NO + NO_2$) removing both the peroxy radicals and NO_x that would otherwise produce O_3 (Horowitz et al., 2007). The yield ($k_3/(k_2+k_3)$) for the IN produced in Reaction (R3) has a significant impact on O_3 production efficiency, as it impacts the magnitude of the chain length, being an important termination step (Horowitz et al., 2007; Wu et al., 2007).

Eight isoprene nitrate isomers (INs), including the Z- and E-isomers of the (1,4)- and the (4,1)-INs, formed from Reactions (R1) and (R3), are shown in Fig. 1 (Chen et al., 1998). For this paper, we apply a short-hand nomenclature for the individual IN isomers, according to which carbon has the OH and ONO_2 groups attached. The first number is the carbon to which the OH is attached and the second number is the carbon to which the ONO_2 is attached. For example, we refer to $HOCH_2C(CH_3)(ONO_2)CH=CH_2$ as the (1,2)-IN. These isoprene nitrates are very reactive because they are still olefinic. Their atmospheric oxidation products, which are

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longer lived than the parent INs because they are saturated, are likely more important than the original nitrate with regard to transportation and deposition (Giacopelli et al., 2005; Horowitz et al., 2007; Paulot et al., 2009b).

The reported yields for total IN production yield range from 4.4% to 15% (Tuazon and Atkinson, 1990; Chen et al., 1998; Chuong and Stevens, 2002; Sprengnether et al., 2002; Patchen et al., 2007). Tuazon and Atkinson (1990) and Sprengnether et al. (2002) determined their reported yields of 8–13% and 12%, respectively, using FT-IR. Chen et al. (1998) utilized a nitrate selective detector to measure the INs using chamber experiments and gas chromatography. They determined a yield of 4.4(±0.8)%. However, they were not able to differentiate between the individual isomers. Chuong and Stevens (2002) used turbulent flow laser induced fluorescence to determine a yield of 15(±10)%. The yield was measured indirectly and has a large uncertainty due to the sensitivity of the simulation approach used for the determination. The most recent reported yields for IN production are 7% (Patchen et al., 2007) and 11.7% (Paulot et al., 2009b). The work of Patchen et al. (2007) was for 100 Torr, and thus the yield at atmospheric pressure may be greater than the 7% reported (Arey et al., 2001). However, individual isomer yields have not been determined because up to this point, no standard has been available.

It has been discussed by Giacopelli et al. (2005) that the lifetimes of the individual INs are likely quite different, and thus the ultimate distribution of isomers in ambient air will reflect both the product yields, and the relative IN lifetimes. Furthermore, it is quite important to note that some isomers may react with OH or O_3 to release NO_2 (Paulot et al., 2009b), which in turn, significantly affects their impact on ambient NO_2 and O_3 concentrations (Horowitz et al., 2007). Thus the determination of the individual isomer product yields is of critical importance.

In this work, we have synthesized three of the isoprene nitrate isomers. They were separated and identified, and their ozone rate constants were determined. Unlike in the field, where only 2 INs have been detected, thought to be the (1,2)-IN and (4,3)-IN (Grossenbacher et al., 2004; Giacopelli et al., 2005), all 8 were detected in

photochemical reaction chamber experiments. Because of this, the total yield and individual yields for each of the 8 INs were determined and their atmospheric lifetimes with regard to OH and ozone were calculated.

2 Experimental

2.1 Synthesis

Three isoprene nitrates, the (1,2)-, (2,1)-, and the (1,4)-INs, were synthesized by adapting the Nichols et al. (1953) procedure. Isoprene monoxide (IM, 2-methyl-2-vinyl oxirane, Aldrich) in anhydrous cyclohexane (99.5%, Aldrich) at a concentration of 0.03 M was cooled to ~15 °C in a 3-neck round bottom flask in an ice bath. The flask was covered with aluminum foil to reduce light exposure and purged with N_2 (grade 5.0, Praxair) as it cooled to minimize water condensation on the inside of the flask. Fuming nitric acid (Aldrich) was added to the flask in a molar ratio of 1:1.5 (HNO_3:IM solution) and then stirred with a stir bar for 30 min. The solution was removed from the flask, stored in a glass amber bottle, and placed in the freezer. Figure 2 shows the synthesis chemistry.

2.2 HPLC separation

The synthesized isoprene nitrates were separated and purified using a Waters 501 HPLC in preparative mode, normal phase, with a Zorbax Eclipse XDB-CN cyano column (4.6×150 mm, 3.5 μm, Agilent), and detected with a Waters 990 photodiode array detector (λ=220 nm). The mobile phase was HPLC grade hexane (Aldrich) at 1 mL min^{-1} that had been dried using anhydrous $MgSO_4$ (Aldrich). For preparative separation, we used a 100 μL stainless steel sample loop. The INs eluted according to increasing polarity and separated in the first 8 min (Fig. 3). Each isoprene nitrate was collected in a separate amber bottle. To further purify the isomers, each isomer solution was re-injected into the HPLC using a 20 μL sample loop and re-collected. Each

individual IN solution was concentrated using N_2 (grade 5.0, Praxair) to evaporate most of the hexane and then stored in a freezer.

2.3 Isoprene nitrate isomer identification

A combination of the synthesis information, HPLC separation and elution order, gas chromatography-electron capture detector (GC-ECD), and GC-MS (EI, CI, and negative CI) data, Gaussian dipole moment calculations, and published mechanistic and theoretical information, was used to identify the synthesized isoprene nitrates. The GC-ECD coupled an HP 5890 Series II GC using a RTX-1701 column (30 m, 0.53 mm i.d., 3.0 µm film thickness, Restek) with a pulsed-discharge electron capture detector (ECD, 220 °C, Valco). A 10 mL stainless steel sample loop and liquid nitrogen column cryofocusing were used to concentrate the INs at the head of the GC column to obtain a detection limit of ~3 ppt. The GC temperature program was as follows: –20 °C for 2 min, 20 °C min^{-1} to 120 °C, 2 °C min^{-1} to 140 °C, held for 9 min, 8 °C min^{-1} to 220 °C, then held for 5 min. The sample inlet and the 10 mL sample loop were heated to 70 °C and 100 °C, respectively, to avoid surface losses. One sample could be injected every 49 min. The GC-ECD inlet, sample loop, and column were conditioned with a large gas phase concentration of the synthesized isoprene nitrates to alleviate adsorptive losses of the INs during experiments.

The ECD detects the isoprene nitrates with very good sensitivity. However, it responds slightly differently to different types of nitrates (Muthuramu et al., 1993) making calibrations difficult without standards, which up to now, have not been available for isoprene nitrates. A relative response experiment was conducted to determine the ECD detector response to an IN with respect to a readily available standard, isobutyl nitrate (IBN, Aldrich). A purified sample of the (1,2)-IN was used to calibrate the GC-ECD. To determine the absolute concentration of the (1,2)-IN in a gas phase standard, we used a custom-made total $RONO_2$ detector, the Total Reactive Nitrogen Instrument (TRENI). This instrument detects organic nitrates using thermal decomposition to produce NO_2, which is then photolytically converted to NO, followed by chemiluminescence-based

detection of the NO. A heated quartz tube inlet (400 °C; Hao et al., 1994; Day et al., 2003) thermally decomposed the IN to NO_2 (Reaction R6). The NO_2 is then converted to NO using a photolytic converter via Reaction (R7). The NO is then reacted with

$$RONO_2 + \Delta \rightarrow RO^{\cdot} + NO_2 \tag{R6}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R7}$$
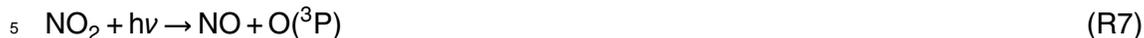
ozone and the resulting photon emitted from the relaxation of the excited state NO_2^* is detected by a photomultiplier tube.

Gas-phase samples of the (1,2)-IN were prepared in a PFA-Teflon bag, and the $RONO_2$ concentration determined using TRENI. Samples of this secondary standard were then injected into the GC/ECD, to produce a calibration curve. The GC-ECD was calibrated at the same time with IBN over a concentration range of 0–50 ppb. The relative response, i.e. S_{IN}/S_{IBN}, was calculated by dividing the slope of the IN calibration curve by the slope of the IBN calibration curve to yield S_{IN}/S_{IBN} = 1.21 (±0.53, 1 s). This was the only IN for which a relative response factor was determined. This value can be compared to those values previously reported for other hydroxy nitrates by Muthuramu et al. (1993). They determined relative response factors (with respect to IBN) for several hydroxy nitrates that ranged from 0.92 for 1-nitroxy-2-hydroxy butane to 2.70 for 2-nitroxy-3-hydroxy butane with an average value of 1.61 (±0.57). For this work, we will assume that the relative response (to IBN) for all of the INs is 1.21, which falls within the uncertainty of the Muthuramu et al. (1993) average value for the α, β-hydroxy nitrates.

A Finnigan GCQ-MS with a RTX-1701 column (30 m, 0.32 mm i.d., 1.0 µm film thickness, Restek) utilized electron impact ionization, chemical ionization, and negative ion chemical ionization to determine the identity of the (1,2)-IN, which was synthesized. The temperature program was the same as for the GC-ECD with the exception that cryo-focusing was not used, and the initial temperature was 40 °C instead of −20 °C.

The dipole moments of each of the 8 IN isomers were calculated using Gaussian 03 at the B3PW91/6–31 g(d) level, which uses Becke's three-parameter exchange and

Perdew-Wang's correlation function (Frisch et al., 2003; Becke, 1993; Perdew et al., 1996) . Structural minima were confirmed using frequency calculations, which yielded no imaginary frequencies. The calculated dipole moments for each IN isomer are listed in Table 1.

2.4 Photochemical reaction chamber experiments

A 5500 L Teflon photochemical reaction chamber was used to determine the yield of INs from the reaction of OH with isoprene in the presence of NO, and is described elsewhere (Chen et al., 1998). The chamber was humidified prior to the yield experiments using a water bubbler to yield a final chamber relative humidity of 25–30%, at ~295 K. NO_2 was added to the chamber (1.25×10^{12} to 2.5×10^{12} molecules cm^{-3}) at the start of the humidification to produce nitrous acid (HONO), which is formed on the walls of the chamber (Akimoto et al., 1987). Isoprene (1.5×10^{13} to 4.5×10^{13} molecules cm^{-3}) and NO (1×10^{13} to 3×10^{13} molecules cm^{-3}) were added to the chamber and allowed to mix. Once mixed, the UV lamps (maximum output at ~370 nm) surrounding the chamber were turned on for 5–30 min intervals, initiating HONO photolysis, and then off during periods of analysis.

Isoprene was determined using a Varian 3300 GC with a PoraPak QS column (6 mm ID stainless steel packed column, Supelco Inc., Bellefonte, PA), separated isothermally at 175 °C, coupled with an FID detector (250 °C, GOW-MAC Instruments Co.). NO, NO_2, and NO_x concentrations were determined using a Chemiluminescence NO-NO_2-NO_x Analyzer (Model 42, Thermo Environmental Instruments Inc, Franklin, MA). A UV Photometric O_3 Analyzer (Model 49, Thermo Environmental Instruments Inc, Franklin, MA) determined ozone concentrations throughout the experiment.

2.5 Ozone rate constant experiments

The rate constants for the reaction of several IN isomers with O_3 were determined using the relative rate method (Atkinson et al., 1986). Ozone was generated using the

ozone analyzer, and added to the chamber first, to a final concentration of 5–120 ppb. Approximately 8–12 mL (yielding ~0.8–1.8 ppb of the three INs) of the synthesized IN solution was then rapidly injected into the chamber. Cyclohexane (anhydrous) from the IN solution (about 400 ppm) was used to scavenge OH radicals produced from the reaction of O_3 with alkenes (Atkinson and Aschmann, 1993; Grosjean and Grosjean, 1998). Crotyl chloride (1-chloro-2-butene, Aldrich), the relative rate reference compound, was injected into the chamber to an initial concentration of 12–85 ppb. The compounds were allowed to mix for 10 min. The peak heights for the 3 INs and for crotyl chloride (CC) were determined throughout the experiment using the GC-ECD.

$$(1/t) \cdot \ln\left\{\frac{IN_0}{IN_t}\right\} = (1/t) \cdot \frac{k_{IN}}{k_{CC}} \ln\left\{\frac{CC_0}{CC_t}\right\} + k_{wl} \qquad (1)$$

Equation (1) shows the relative rate equation, including the impact of wall loss for the INs, where k_{wl} is the appropriate first order IN wall loss rate constant (s^{-1}). IN_0, CC_0, IN_t, and CC_t are the

$$IN_i + O_3 \rightarrow loss \qquad (R8)$$

$$CC + O_3 \rightarrow loss \qquad (R9)$$

concentrations of each IN isomer and CC at time t_0 and t, respectively. The IN rate constants were determined by plotting $(1/t) \cdot \ln\left([IN]_0/[IN]_t\right)$ vs. $(1/t) \cdot \ln\left([CC]_0/[CC]_t\right)$ producing a slope equal to k_8/k_9 and an intercept equal to k_{wl}. The CC reference ozone rate constant is $2.29(\pm 0.17) \times 10^{-17}$ cm^3 molecules^{-1} s^{-1} (Johnson et al., 2000).

3 Results and discussion

Isoprene nitrate identification

The synthesized isoprene nitrates were separated using normal phase liquid chromatography. From the mechanism, it is possible to produce only the (1,2)-IN, the

(2,1)-IN, and the (1,4)-INs. The HPLC peaks labeled A–C in Fig. 3 were determined to be IN isomers. The absorption spectra for these three peaks, obtained from the HPLC diode array detector, are similar to each other and to a reference alkyl nitrate, IBN, indicating that peaks A–C are organic nitrates. Given an expected elution order of in-
5 creasing polarity, as expressed from the calculated dipole moments, peaks A, B, and C in Fig. 3 can be identified as the E-plus Z-(1,4)- (unseparated), the (2,1)-, and the (1,2)-INs, respectively. The shoulder of Peak A (not always resolved) could be one of the Z- or E-isomers of the (1,4)-IN. Peak C was completely separated from the rest of the synthesized INs by preparative HPLC. Peaks A and B could not be completely isolated,
10 based on analysis of the GC chromatograms for the HPLC-separated peaks, even though they were completely separated in the HPLC chromatogram (Fig. 3). Peak C is identified as the (1,2)-IN using the dipole moment calculations and the GC-MS analysis of the purified IN. Specifically, the (2,1)- and the (1,4)-IN can have an α-cleavage that would produce a 76 m/z fragment ($^+CH_2$-ONO_2), which is typical for primary nitrates
15 (Luxenhofer et al., 1994; Schneider et al., 1998; Fischer et al., 2000). In contrast, the (1,2)-IN cannot produce that fragment, and the GC/MS spectrum for that peak did not yield a fragment at $m/z=76$. We therefore identified peak C in Fig. 3 as the (1,2)-IN.

A major objective for this study was the determination of the yields of the individual IN isomers. The GC peak assignments were conducted in part by compar-
20 ing chromatograms from the total synthesized IN sample (Fig. 4) with that from an isoprene/NO$_x$ irradiation chamber experiment (Fig. 5). The peaks in Fig. 4 labeled A–C correspond to the same peaks in the HPLC chromatogram in Fig. 3. The peaks labeled 1–8 in the chamber experiment (Fig. 5) are identified as the INs. The peaks between 20 and 25 min are products of the direct NO$_2$ reaction with isoprene, as dis-
25 cussed in Chen et al. (1998). All of the peaks that eluted before 10 min were present before the experiment began, eliminating them as possible INs. The IN peaks 5, 6, and 8 in Fig. 5 correspond to the HPLC peaks A, C, and B, respectively. Peak 6 is the (1,2)-IN because the peak matches up with the GC peak of the purified IN that was identified as the (1,2)-IN by GC-MS analysis. The INs should elute from the GC

column in approximate order of polarity from the semi-polar column phase, suggesting that the (1,4)-IN should elute before the (2,1)-IN (see Table 1). Therefore, peak 5 is assigned to one of the (1,4)-IN isomers, specifically the E-isomer. The E-(1,4)-IN has a smaller dipole moment (2.7903) than the Z-(1,4)-IN (3.2539) and would elute first from the HPLC column (peak A). Similarly, we assign peak 8 in Fig. 5 to the (2,1)-IN isomer.

Our peak identification assumes that the Z/E isomers are separable. To examine this, an alkene nitrate (1-nitroxy-1-propene) was synthesized using 1-bromo-1-propene (Aldrich) and $AgNO_3$ (Aldrich). The resulting Z- and E-nitrates were injected onto the GC column to determine whether they could be separated, and if so, to what extent. The data show that the nitrates can be separated by the GC column, in this case, by 30 s. By analogy, the Z-(1,4)-IN isomer should be separated from the E-(1,4)-IN already identified as peak 5 in Fig. 5. Because peak 6 has already been identified as the (1,2)-IN, this leaves peak 4 as the only possible choice for the Z-(1,4)-IN isomer. Paulot et al. (2009b) discussed that the Z-isomer will be dominant over the E-isomer, which is consistent with the yield data discussed below. The (3,4)-IN isomer is assigned to peak 7 in Fig. 5, because two of the isomers, the (2,1)-IN and the (3,4)-IN should have very small yields (Giacopelli et al., 2005), and the (2,1)-IN is already identified, as discussed above. The (2,1)-IN and (3,4)-IN should have the lowest yields due to the instability of the primary carbon centered radical (Lei et al., 2001; Giacopelli et al., 2005). Because the (2,1)-IN has already been assigned to peak 8, the (3,4)-IN is assigned to peak 7.

The identification of the 3 remaining INs, the (4,3)-IN and the two (4,1)-IN isomers, is tentative. Based on the fact that the (3,4)- plus the (4,3)-RO_2 yield (discussed below) has to be at least as large as the methacrolein (MACR) yield of 27% (Karl et al., 2006), since MACR is derived from those radicals, and since the (4,3)-RO_2 yield is believed to be much larger than the (3,4)-RO_2 yield (Lei et al., 2001; Giacopelli et al., 2005; Paulot et al., 2009b), the only IN that satisfies this latter requirement (along with peak 7) is peak 2 in Fig. 5. Peak 2 is thus assigned to the (4,3)-IN. The remaining 2 IN peaks, peaks 1 and 3 in Fig. 5, are assigned to the Z- and E-(4,1)-IN isomers, respectively.

3.1 Isoprene nitrate yields

The total and individual isoprene nitrate yields were determined using GC-ECD and the photochemical reaction chamber. Isoprene and NO were added to the humidified chamber and the GC-ECD was used to determine the concentration of each isoprene nitrate over time during the irradiations. Using the ECD relative response factor ($1.21 \times S_{\text{isobutyl nitrate}}$) for the INs, the individual and total concentrations of the 8 INs were calculated over the course of the yield experiment. The IN concentrations were corrected for IN consumption by OH, as described in Atkinson et al. (1982b). The average correction factor was $1.12(\pm 0.10)$. For any individual nitrate, IN_i, we have the following reactions accounting for individual isomeric IN production.

$$OH + isop \rightarrow \gamma_i \cdot RO_{2,i} \tag{R10}$$

$$RO_{2,i} + NO \rightarrow RONO_{2,i} \tag{R11a}$$

$$\rightarrow RO_i + NO_2 \tag{R11b}$$
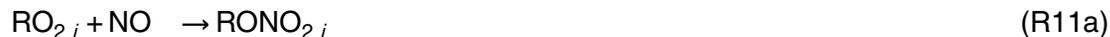
Here γ_i is the fractional yield of the appropriate precursor peroxy radical. Since, assuming steady state in $RO_{2,i}$, and where "R" represents the reaction rate, $R_{10} \cdot \gamma_i = R_{11}$ and $R_{10} = k_{10}[OH][isop]$ and Eq. (2) then describes the isoprene decay rate. The rate of appearance of

$$-d[isop]/dt = R_{11}/\gamma_i = k_{11}\left[RO_{2,i}\right][NO]/\gamma_i \tag{2}$$

$$d\left[RONO_{2,i}\right]/dt = R_{11a} = k_{11a}\left[RO_{2,i}\right][NO] \tag{3}$$

$RONO_{2,i}$ is described by Eq. (3), and thus if we plot $\Delta[RONO_{2,i}]$ vs. $-\Delta[isop]$, the slope $= k_{11a}[RO_{2,i}][NO]/(k_{11}[RO_{2,i}][NO]/\gamma_i) = \gamma_i \cdot k_{11a}/k_{11}$. Thus if γ_i is known, the branching ratio, $\alpha_i = k_{11a}/k_{11}$, for $RONO_{2,i}$ formation, can be determined. If we plot $\Delta\Sigma[RONO_{2,i}]$ vs. $-\Delta[isop]$, the slope is equal to the overall average (γ-weighted) branching ratio, R_{11a}/R_{11}. The results for such a plot for all experiments are shown

in Fig. 6, revealing a slope of 0.070±0.009(1 s). The individual isomers' concentrations were plotted versus the loss of isoprene to obtain the individual yields, which are listed in Table 1.

The relationship between size and structure of molecules and the branching ratios has been studied for simple molecules, but for multiply functionalized RO_2 radicals, it is complex, and our understanding is quite limited (Espada and Shepson, 2005). We first note that three products, which we identify (see below) as the (1,2)-IN, the (4,3)-IN, and the Z-(4,1)-IN, represent 90% of the total IN yield. The Paulot et al. (2009b) study reports 61% of the total from these three isomers. Our reported overall yield is considerably greater than that (0.044) determined by Chen et al. (1998), using similar techniques. We attribute this to sampling losses, avoided here through "conditioning" of the sampling system with actual gas phase IN samples. However, given our previous experience of the potential for losses, and given the calibration uncertainty, we report a conservative asymmetric uncertainty for the total yield as 0.070 (+0.025/−0.015). Our total IN yield value agrees well with that of Patchen et al. (2007), who also obtained an overall yield of 0.07, although at a total pressure of 100 Torr. This result then implies that 100 Torr is above the high pressure limiting value for the organic nitrate yield. Paulot et al. (2009b) derived an overall yield of 0.117, using their combined measurement and modeling approach. Giacopelli et al. (2005) calculated an overall yield of 0.086, based on structure-yield information from various literature information. Sprengnether et al. (2002) obtained the value 0.12, while the original estimate from Tuazon and Atkinson (1990) was 0.08–0.13. It is clear that the range of values for this quantity is converging, with a current average reported yield of ∼0.09±0.02. We note that while we observe that the (1,2)-IN is ∼31% of the total IN yield, Chen et al. (1998) observed that this peak was 45–65% of the total IN yield. In contrast, Paulot et al. (2009b) assume that the (1,2)-IN is 24% of the total IN yield, a bit smaller than our measured value.

In Table 1 we list the individual calculated yields, from the plots of $\Delta[RONO_{2,i}]$ vs. $-\Delta[isop]$. As discussed in Giacopelli et al. (2005), based on the work of Espada

and Shepson (2005), we previously estimated that the branching ratio, α_i, for α, β-hydroxyperoxy radicals for isoprene is ~0.058, and for the δ-hydroxyperoxy radicals, 0.15. If we accept these values for α_i, we can calculate values for the yield of each precursor $RO_{2,i}$, γ_i; the results are shown in Table 1. We also show in Table 1 the values for γ_i assumed by Paulot et al. (2009b). We can alternatively use the Paulot et al. (2009b) values for γ_i, and derive the corresponding values for α_i; these are also shown in Table 1. The combination of these derived values are then useful for evaluation of the individual isomer identification.

The principal uncertainty in isomer identification is in the identities for peaks 1 and 2. We assigned these to the Z-(4,1)-IN and the (4,3)-IN, respectively. With these assignments, we calculate γ_i values of 0.045 and 0.61, respectively, for the corresponding RO_2 precursor yields. While the latter value seems too large, if we reverse the assignments, the RO_2 yields become 0.12 and 0.24, respectively. In this latter case, the sum of the (4,3)-RO_2 and (3,4)-RO_2 yields would be 0.245, which is less than the published yield for methacrolein (MACR) of 0.27, which is not possible. Also, if we switch our assignment of peaks 1 and 2 to the (4,3)-IN and Z-(4,1)-INs, respectively, we would calculate α_i values, using the Paulot et al. (2009) γ_i values, of 0.029 and 0.30, respectively, both of which seem unreasonable, compared to the values shown given our assignments, in Table 1. Thus, we believe that these are the only assignments that can be made that are consistent with the literature information. It should be noted that our calculated value for $\Sigma\gamma_i$=115%, a reasonable result of the propagation of the uncertainties in this analysis. We note that the calculated γ_i values for the (1,2)-RO_2 and (2,1)-RO_2 radicals are 0.38 and 0.029, for a total of 0.41, in good agreement with the values (0.41 and 0.02) used by Paulot et al. (2009b), and consistent with the published MVK (which derives from these two radicals) yield of 0.41 (Karl et al., 2006). It thus appears from the calculated α_i values in Table 1 that there are factors influencing the range of individual α_i values for $RONO_2$ production that are not yet understood.

3.2 Isoprene nitrate lifetimes

In Fig. 7 we present the combined data from 7 experiments for the (1,2)-IN and the (2,1)-IN and 6 experiments for the E-(1,4)-IN for the determination of the ozone rate constants. Using the rate constant for O_3 reaction with crotyl chloride, the slopes yield values of 0.53, 1.06, and 3.4×10^{-16} cm^3 molecule^{-1} s^{-1}, which are very fast ozonolysis rate constants, corresponding to lifetimes against ozonolysis of 5, 2.6, and 0.8 h, for the E-(1,4)-IN, (1,2)-IN, and (2,1)-IN, respectively, for 40 ppb of O_3. These values are very large compared to the numbers assumed in Paulot et al. (2009b), and larger for the external olefinic INs, which is surprising. However, Paulot et al. (2009b) discuss that it appears that the nitrooxy group can increase the reactivity of double bonds to addition. We can estimate the individual IN isomer lifetimes with respect to ozone and OH using the ozone rate constants determined in this work and the OH rate constants calculated from the method of Kwok and Atkinson (1995). Because only 3 of the ozone rate constants were determined, an average value of 1.7×10^{-16} cm^3 molecule^{-1} s^{-1} was used for the remaining 5 INs. However, the (4,1)-IN isomers should have similar rate constants to those for the (1,4)-IN isomers, and thus for those isomers, we also calculated the lifetimes assuming they are the same as for the (1,4)-IN ozone rate constant. Assuming that $[OH]=1\times10^6$ and $[O_3]=1\times10^{12}$ molecules cm^{-3}, the lifetimes for the isomers vary from 45 min. for the (2,1)-IN to two h for the (1,2)-IN, as shown in Table 1. It is thus clear that the isoprene nitrates themselves will be relatively fleeting in the atmosphere, and will be quickly converted (if not lost by dry or wet deposition; Shepson et al., 1996) to either more complex multifunctional (highly water soluble and adsorptive) organic nitrates and/or dinitrates, or will recycle NO_2 upon oxidation, as discussed by Giacopelli et al. (2005), Horowitz et al. (2007), and Paulot et al. (2009b). It is thus highly important that the fraction of NO_x that is recycled upon reaction with OH and O_3 be studied, at least for the three most important IN isomers.

In this work we were able to identify and quantify the individual isoprene nitrate isomers. We were able to synthesize, separate, and identify 3 of the 8 INs and determine

their ozone rate constants. The total and individual yields for the INs were determined. The total IN yield is within the literature values and is similar to the most recently reported value of 7% (Patchen et al., 2007). The relatively short lifetime of the INs suggest that they act more like an intermediate product in the formation of less reactive dinitrates and carbonyl nitrates (Paulot et al., 2009b). They can either retain or release the NO_x, thus making the nature of the products of the INs reaction with OH and O_3 important and worthy of further study. The methods described here for synthesis, purification and identification should help in enabling that study.

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Table 1. Isoprene nitrate data. The peak numbers represent the peaks labeled in Fig. 5 and in the IN identification in the Results and Discussion section. [a]The (4,1)-IN isomers have 2 values for their lifetime. The lower value represents the lifetime using the average ozone rate constant $(1.67 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1})$. The higher value represents the lifetime if we assume that the (4,1)-IN isomers have a similar ozone rate constant to the (1,4)-IN.

Peak Number	Average Retention Time (min)	IN Identification	Dipole Moments	Absolute Yield	Relative Yield (%)	Ozone Rate Constant $(cm^3\ molec^{-1}\ s^{-1})$ $\times 10^{-16}$	Calculated Relative RO_2 Yield (γ)	Paulot et al. (2009b) γ	Lei et al. (2001) Calculated Relative RO_2 Yield (γ)	Atmospheric Daytime Lifetime (h)[a]	Calculated α_i using Paulot et al. (2009b) γ_i
1	12.47	Z-4,1	2.9804	0.0067	9.38	–	0.045	0.12		1.97 or 1.07	0.055
2	13.1	4,3	3.9387	0.0356	49.9	–	0.61	0.23	0.29	1.25	0.15
3	14.21	E-4,1	2.8789	0.0028	3.92	–	0.019	0.021		1.97 or 1.07	0.13
4	15.00	Z-1,4	3.2539	0.0015	2.10	–	0.010	0.13		1.92	0.01
5	17.18	E-1,4	2.7903	0.0007	0.98	0.53(±0.099)	0.005	0.022		1.92	0.03
6	18.44	1,2	4.0902	0.0221	30.9	1.06(±0.11)	0.38	0.41	0.34	2.01	0.053
7	30.43	3,4	3.5916	0.0003	0.42	–	0.052	0.05	0.05	1.22	0.0059
8	32.33	2,1	3.7383	0.0017	2.38	3.42(±0.43)	0.029	0.02	0.02	0.75	0.083
						Z- plus E-(1,4)	0.015	0.15	0.22		
						Z- plus E-(4,1)	0.063	0.14	0.08		

Fig. 1. Isoprene nitrate isomers.

Fig. 2. Isoprene nitrate synthesis chemistry.
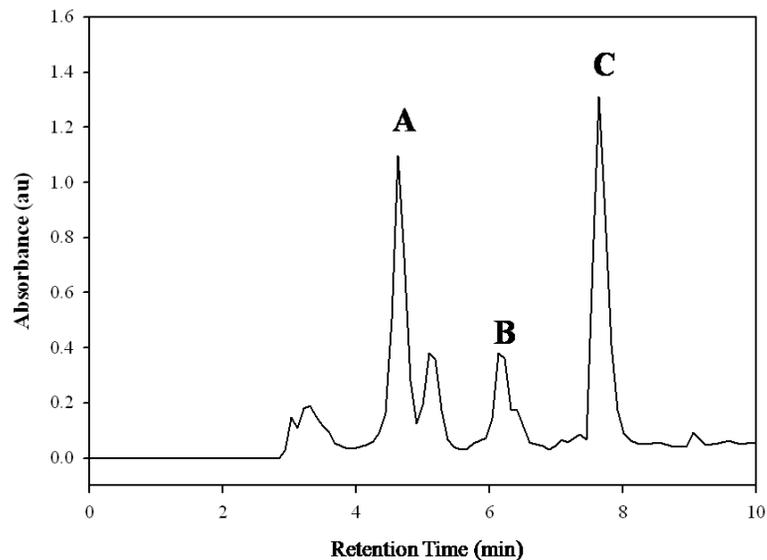
**Fig. 3.** HPLC chromatogram of the synthesized INs. The peaks labeled A–C represent the individual IN isomers.
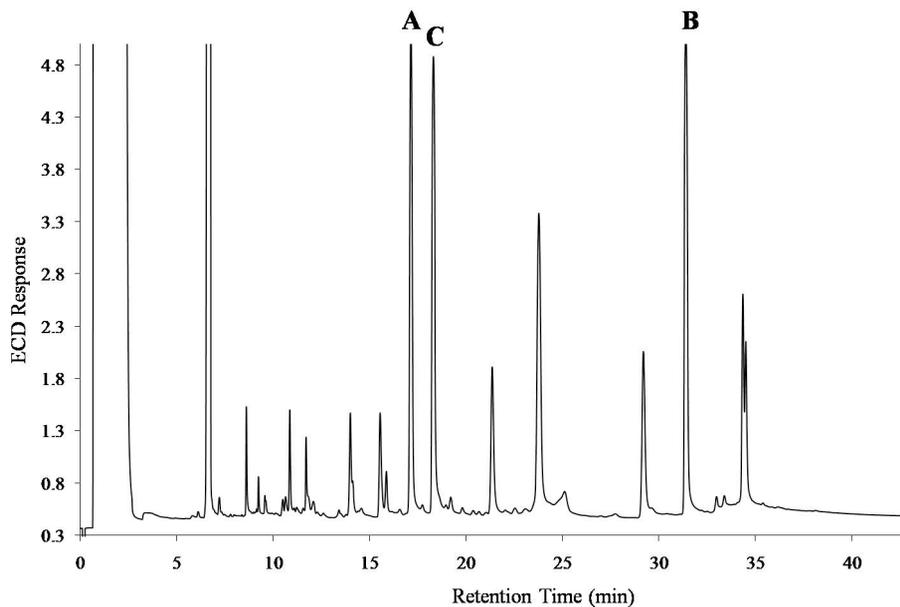
**Fig. 4.** GC-ECD chromatogram of the synthesized INs. The peaks labeled A–C correspond to the INs with the same label in Fig. 3.
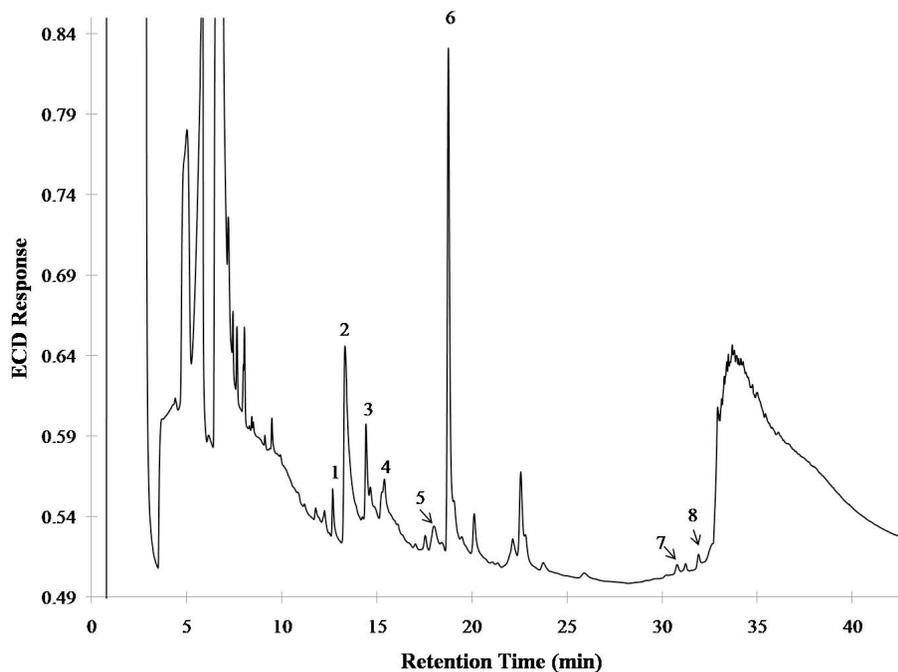
Fig. 5. GC-ECD chromatogram of an isoprene/NO$_x$ yield experiment. The numbers correspond to the INs produced in the yield experiment.
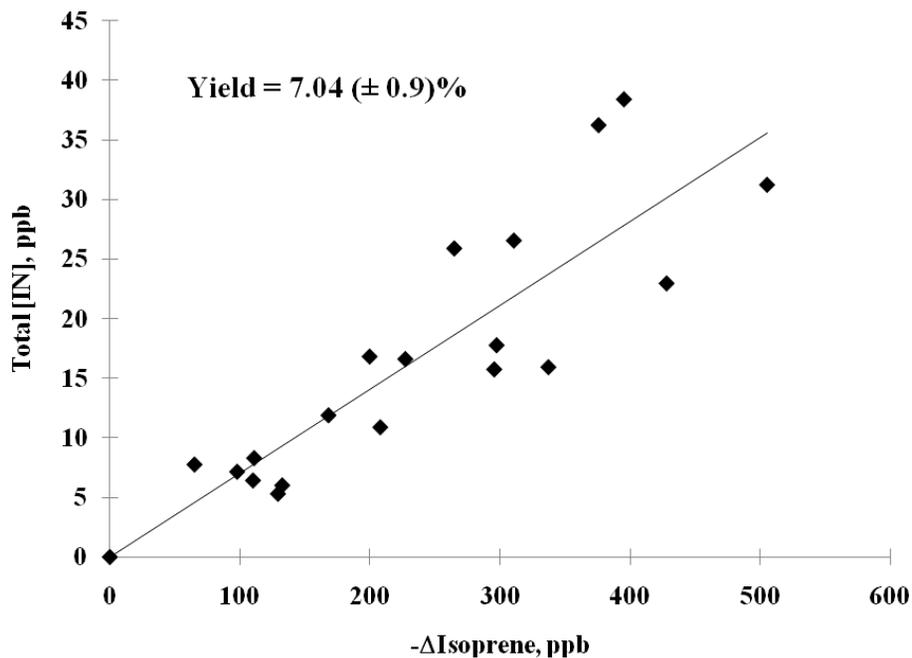
Fig. 6. Total isoprene nitrate yield. Total [IN] is plotted vs. the loss of isoprene over time. The data plotted are from multiple experiments. The uncertainty represents 1 s.
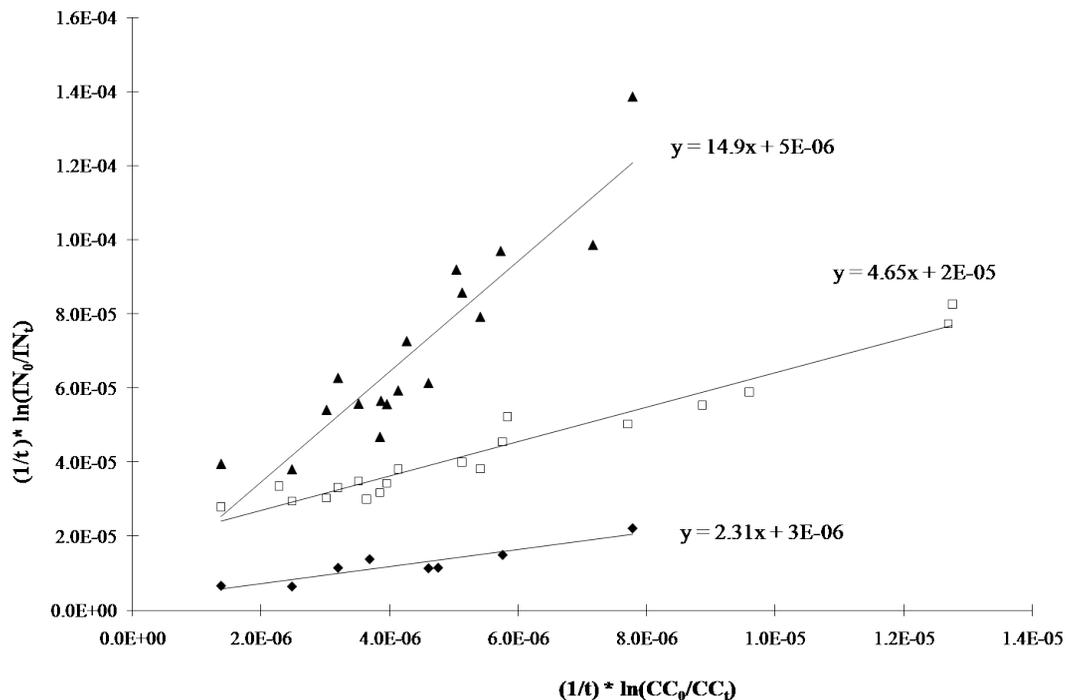
Fig. 7. Ozone rate constant data for three isoprene nitrate isomers. Triangles = (2,1)-IN, squares = (1,2)-IN, and diamonds = E-(1,4)-IN.